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Low Temperature Sintering of $Pb(Zr,Ti)O_3$ Ceramics with $BiFeO_3$ and $Ba(Cu,W)O_3$ Additives

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We have succeeded to lower the sintering temperature of the $Pb(Zr,Ti)O_3$ ceramics by an addition of $BiFeO_3$ and $Ba(Cu,W)O_3$. Microstructural and compositional analyses revealed an existence of a continuous amorphous phase at the grain boundaries composed of lead and copper oxides. Therefore, the densification of the ceramics at the low temperature of 935° C is promoted by a formation of liquid phase which originates from this amorphous layer. Furthermore, an adoption of the ball-milling method have reduced the sintering temperature down to 900° C.

1. Introduction

The application of $Pb(Zr,Ti)O_3$ ceramics to various fields of electronic devices have been developed because of its superior electrical properties, particularly piezoelectricity. But the volatilization of PbO during high temperature sintering (>1200 ℃) causes troubles in compositional fluctuation and the environmental contamination. The lowering of the sintering temperature of $Pb(Zr,Ti)O_3$ ceramics can also offer the advantage to the reduction of energy consumption and fabrication cost.

We attempted a combined use of two perovskite-type complex-oxides, $BiFeO_3$ (abbreviated as BF) and $Ba(Cu_{0.5}W_{0.5})O_3$ (BCW), as an additive to lower the sintering temperature of 0.5 wt% MnO_2-added $Pb(Zr_{0.53}Ti0_{0.47})O_3$ ceramics (PZT), and succeeded to sinter this ceramics at 935℃ for 60 min [1]. Furthermore, we investigated the effects of these two additives on the morphotropic phase boundary (MPB) of $Pb(Zr,Ti)O_3$ ceramics and determined the optimum Zr/Ti ratio to be 52/48 [2].

In this paper, the results of microstructural and compositional analyses on the low-

temperature sintered PZT are presented and the densification process of this ceramics is discussed. An attempt to lower the sintering temperature further by an adoption of the ball-milling method is also described.

2. EXPERIMENTAL

2.1. Sample preparation

The commercially available reagent grade metal oxides were used as raw materials, and PZT and BCW were separately synthesized by heating at 870 ℃ for 2 h, followed by pulverization. All PZT, BCW, Bi_2O_3, Fe_2O_3 and CuO were weighed according to 0.92PZT-0.05BF-0.03BCW including excess 0.08 wt% of CuO (PZT-C'), and then mixed in an agate mortar. Disk samples of 10 mm diameter and 3 mm thickness were uniaxially pressed at 800 kg/cm^2, and then sintered isothermally with a heating rate of 5 ℃ /min at a temperature between 850℃ and 1250℃ for a period between 30 min and 2 h.

2.2. Characterization

The morphology of the cross section of sintered body was observed by using a JSM-T330A scanning electron microscope (SEM). A JEM-2000FXII transmission electron microscope (TEM) equipped with an energy dispersive X-ray spectrometer (EDS) also was used for the microstructural analyses. Thermal mechanical analysis (TMA) was performed to detect a shrinkage of compacted body during the heating process with a heating rate of 5℃/min by using a Rigaku Thermoflex 8141 H Dielectric (1 kHz) and piezoelectric measurements were carried out by using an impedance analyzer (YHP4194A) after being polarized under 2 kV/mm bias at 130℃ in a silicone oil bath for 20 min. Density of sintered body was determined by means of an Archimedes method.

3. RESULTS

3.1. Microanalyses

The results from TEM observation and EDS analysis [3] of the grain boundary of PZT-C' ceramics are shown in Fig. 1. The grain boundary of about 25 nm width is observed clearly between two grains in the ceramics (Fig. 1(a)). The X-ray intensities of Pb and Cu in the vicinity of the grain boundary become higher than those in the matrix, but that of Fe become lower, and those of Zr and Ti over 200 nm width on both sides of the grain boundary almost invariable (Fig. 1(b)).

3.2.Shrinkage curve

Isothermal shrinkage of PZT and PZT-C' ceramics were measured after being sintered at temperatures of 1250°C and 935°C, respectively, and cooled immediately to room

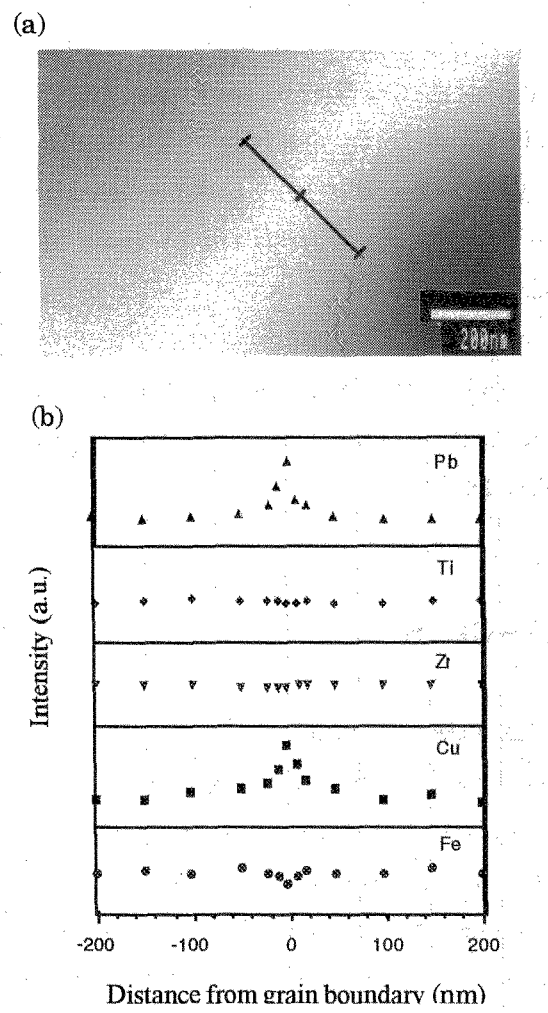

Fig. 1. (a) TEM micrograph of grain interface and (b) EDS analysis.

temperature (Fig. 2). Generally, the relation between shrinkage and time can be expressed as $\Delta L/L=kt^n$, where ΔL is a difference of the length of sample before and after sintering, L the initial length of sample, k and n the constants, and t the sintering time. The shrinkage curve of PZT is divided into two stages. The index n=0.40 (t<25 min) obtained here is known as a solid state

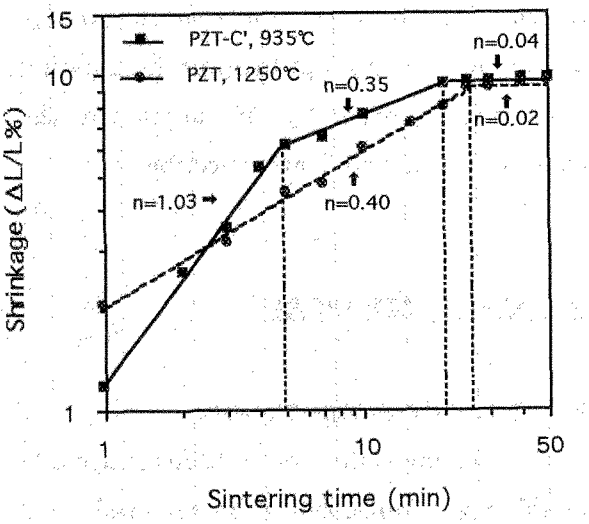

Fig. 2. Isothermal shrinkage curves.

sintering due to the bulk diffusion [4,5]. The index n=0.02 (t>25 min) on the second stage is considered to be a grain growth. On the other hand, there are three stages for PZT-C', which suggests a different process from that of PZT; i.e., n=1.03 between 1 to 5 min is considered to be an arrangement of grains, n=0.35 from 5 to 20 min the solution-precipitation or the grain boundary diffusion of atoms [6-8] and then n=0.04 over 20 min the grain growth.

4. Discussion

It is indicated from the microanalyses that the principal components of the amorphous grain boundary of PZT-C' are PbO and CuO. The segregation of PbO into the grain boundary of $Pb(Zr,Ti)O_3$ ceramics has been already found [10,11] and the addition of CuO

Table. Electrical properties and density for PZT-C's sintered under various temperatures and times.

Sintering Temp. (°C)	Sintering time(min)	Kp (%)	Qm	$\varepsilon^{T}_{33}/\varepsilon_{0}$	d_{31} ($\times 10^{-11}$ m/V)	tan δ (%)	ρ_a (g/cm^3)	ρ_b (g/cm^3)
880	90	42.5	674.8	724.9	60.3	2.3	7.93	7.91
	120	42.5	498.2	873.7	78.4	2.1	7.91	7.88
890	60	46.4	534.6	739.5	64.8	2.0	7.93	7.91
	90	47.1	706.1	627.3	61.8	2.0	7.94	7.90
	120	47.5	646.9	709.9	67.7	3.07	7.91	7.87
900	60	47.9	526.3	750.4	68.5	1.8	7.91	7.89
	90	49.1	410.3	923.1	79.7	2.5	7.91	7.89
	120	42.0	385.8	883.2	67.7	2.6	7.90	7.89
935	90	50	649.5	698.2	69.4	1.8	7.88	7.84

lowered the sintering temperature of $BaTiO_3$ ceramics due to the formation of a liquid phase [11,12]. Thus, it is concluded that the densification of PZT-C' is enhanced by the liquid phase composed of PbO and CuO as deduced from the shrinkage behaviors.

In order to clear the above densification process, the ball-milling method is introduced because it realize the homogeneous particle size and compositional distribution during the mixing process. The electrical properties and densities are summarized in Table for PZT-C's sintered at various temperatures and for various times. The results suggest that PZT-C' can be sintered at a lower temperature than 935° C by the ball-milling method.

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